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High Temperature Stability of Oxygen Functionalized Epitaxial Graphene/Metal Contact Interfaces

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Abstract. The electrical characteristics of oxygen functionalized epitaxial graphene and Ti/Au metal contact interfaces were systematically investigated as a function of temperature. As the temperature was increased from 300 K to 673 K, the contact resistance and the sheet resistance decreased by 75% and 33%, respectively. The resistance of oxygen functionalized graphene vs temperature exhibited Arrhenius type behavior with activation energy of 38 meV. The results showed no hysteresis effects in resistance measurements over the temperatures studied here, suggesting the contact interfaces remain stable at high temperatures.

Introduction

Surface functionalization of graphene with different reactive species has been extensively studied to modulate its electrical, chemical and mechanical properties for a wide range of applications [1,2]. For example, functionalization of graphene was shown to enhance the sensitivity of the graphene sensor without significantly reducing its conductivity [3]. It has also been shown that covalently modifying the graphene sp^2 structure with functional groups such as oxygen, can not only can change the charge carrier type and concentration in graphene, but also induce a bandgap of over 1 eV, enabling a plethora of potential electronic applications [4]. However, the performance of electronic devices greatly depends upon the nature and quality of deposited metal contacts. Poor quality of contacts can result in high contact resistance, R_C, which limits the on-state current of graphene field-effect-transistors and can degrade the performance of devices significantly [5]. Understanding and controlling the electrical characteristics of metal-functionalized graphene interfaces is therefore an important aspect of contact engineering for high speed switching applications.

While there have been several experimental and theoretical studies explaining the nature of interaction between metal and pristine graphene [5,6], so far, very little attention has been paid towards the effect of functionalized graphene films on metal contacts. Although studies have shown the presence of oxygen between the graphene and metal contacts improve R_C [7] and heat transport [8], the high temperature behavior of R_C, and sheet resistance, R_{sh}, of oxygen functionalized graphene/metal contacts has not been discussed to-date. In this work, we investigate the high temperature stability of Ti/Au metal contacts on the oxygen functionalized epitaxial graphene films grown on 6H–SiC (0001). The transfer length method (TLM) was used to extract the R_C and R_{sh} of functionalized graphene films at temperatures between 300 K and 673 K. Surface characterization techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to monitor the changes in the functionalized graphene film.

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Experimental Details

The epitaxial graphene films were synthesized on 8x8mm^2 semi-insulating 6H–SiC (0001) substrates (II-VI, Inc.) by sublimation of Si at 1540˚C in an argon environment for 30 min. These films are naturally n-type, with typical sheet carrier concentrations of 5–10x10^{12} cm^{-2} due to the induced charge transfer from underlying unsaturated Si-bonds near the SiC interface [9]. The functionalization of graphene with oxygen was performed at room temperature using electron-beam generated plasmas produced by injecting a 2 keV electron-beam into an O_2/Ar gas mixture with a 5% O_2 flow rate at a total pressure of 75 mTorr [10]. This approach limits the kinetic energy of ions at the sample surface to less than ≈ 3 eV. The total treatment time was 60 s with a plasma exposure time of 6 s, which resulted in oxygen surface coverage of ≈ 4.5 atomic % determined by XPS. Additional details on the sample preparation procedure, graphene growth morphology and the operation of plasma reactor are described elsewhere [1,9]. Following graphene growth and functionalization, TLM structures consisting of 150 µm wide (W) and 100 µm long (L) contacts (Fig. 3 inset) were fabricated by conventional photolithographic techniques using AZ5214E photoresist. The channel length (d) of the TLM structures varies from 5 µm to 45 µm, in steps of 5 µm. Ti/Au (10 nm/100 nm) metal films were deposited using e-beam evaporation followed by lift-off in warm acetone (≈ 45˚C). In order to minimize the photo-resist contamination, the sample was annealed in vacuum at 400˚C for 30 min using rapid thermal annealing after metal deposition. A Thermo Scientific K-Alpha XPS was used for chemical analysis of the graphene and the structural changes were observed by Raman spectroscopy (Renishaw InVia Raman microscope) with an excitation wavelength of 514.5 nm, laser spot size of 5 µm and an incident laser power of 20 mW. The Savitzky-Golay smoothing was used to reduce noise effect of the acquired spectra. All electrical measurements were performed under ambient conditions at temperatures between 300 K and 673 K using a Cascade Microtech probe station and a Keithley 4200 semiconductor parameter analyzer.

Results and Discussions

Fig. 1 shows the XPS C1s spectra of as-grown and oxygen functionalized epitaxial graphene. The untreated graphene exhibited two major peaks at 283.8 eV and 284.5 eV, corresponding to Si-C and C–C (sp^2) bonding, respectively. Following oxygen plasma treatment, a clear change in the chemical composition of graphene was observed with a broadened C1s peak and a drastic decrease in the sp^2 bonding peak intensity due to the presence of C–O (286 eV), C=O (287 eV) and O–C=O (288 eV) functional groups. Analysis of high resolution XPS spectra confirmed the surface coverage of oxygen to be approximately 4.5 atomic %. The addition of oxygen atoms changes some of the sp^2–hybridization of graphene to sp^3–hybridization, modifying its electrical and chemical properties.

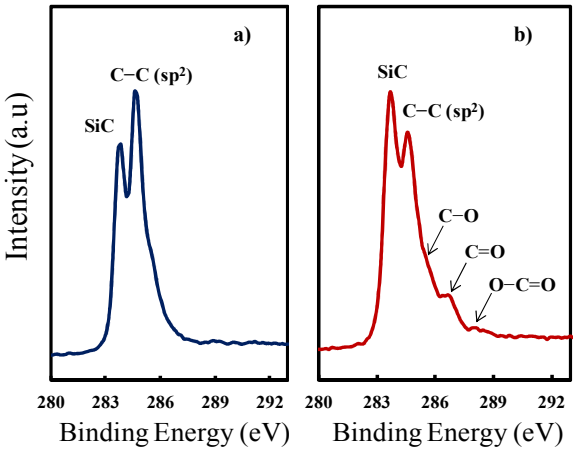

Fig. 1. XPS C1s spectra of a) as-grown graphene and b) oxygen functionalized graphene at 75mT using O_2/Ar plasma.

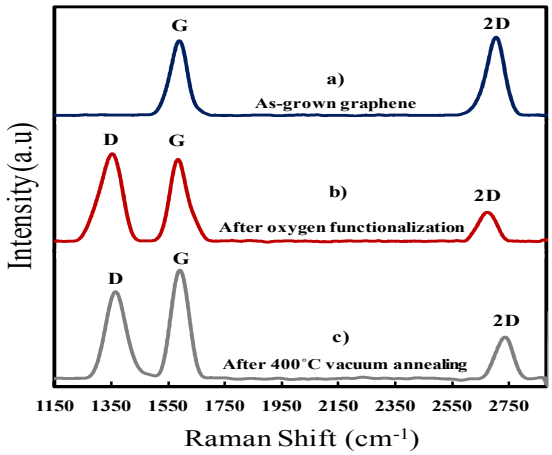

Fig. 2. Raman spectra of graphene at different processing steps a) as-grown b) functionalized and c) annealed

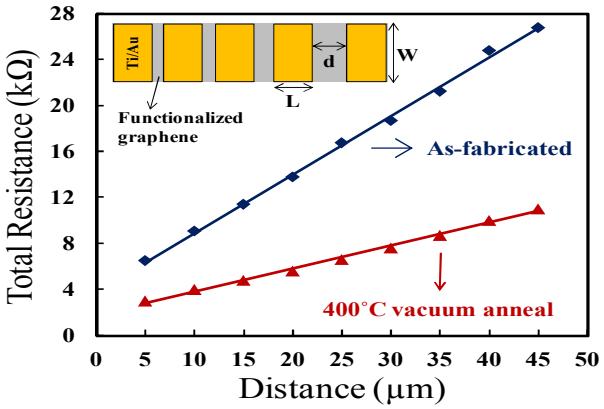

Fig. 3. TLM linear fit of total resistance against varying channel lengths both before and after vacuum annealing. Inset shows top view of TLM metal contacts.

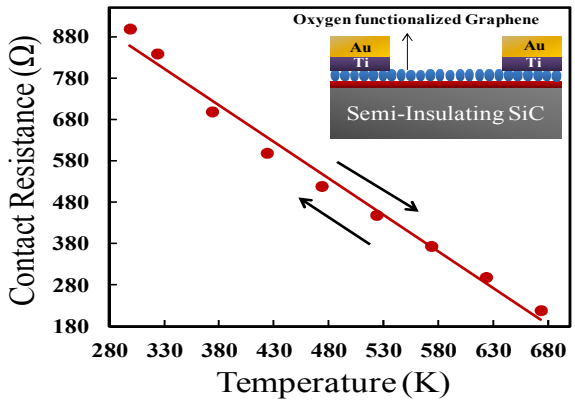

Fig. 4. Temperature dependence of Ti/Au contact resistance. Inset shows side view of oxygen functionalized graphene/metal contact interface.

The structural changes in the epitaxial graphene were investigated by Raman spectroscopy as shown in Fig. 2. The as-grown graphene exhibited a G-peak at 1598 cm^{-1} and a 2D-peak at 2741 cm^{-1}, the latter having a full width half maximum (FWHM) of ≈ 63 cm^{-1}, indicating the average thickness of the graphene film for the probed area to be two monolayers [9]; this was further verified by XPS analysis. After oxygen functionalization, an intense disorder induced D-peak was observed at 1355cm^{-1} and the 2D-peak was strongly suppressed. The disorder induced ratio (I_D/I_G) and the FWHM of D-peak were calculated as 1.06 and 86 cm^{-1}, respectively, demonstrating structural modifications to the graphene sp^2 character. From the I_D/I_G ratio, the average domain size, L_a, was estimated to be 16 nm using the expression given by Pimento et al [11].

Hall measurements showed the p-type nature of the oxygen functionalized graphene with a carrier density of 5.6x10^{13} cm^{-2}, in contrast to the n-type nature of the non-functionalized sample. Linear current-voltage (I–V) characteristics were observed between Ti/Au and oxygen functionalized graphene, implying ohmic contact behaviour. Fig. 3 shows a typical TLM linear fit of total resistance measured for as-fabricated and vacuum annealed (400˚C) Ti/Au contacts as a function of 'd'. At 300 K, the R_{sh}, R_C and contact resistivity (ρ_C) of the functionalized graphene were calculated as 76.3 kΩ/sq, 1.91 kΩ, and 1x10^{-2} Ω-cm^2 respectively. When the sample was subjected to vacuum annealing, R_{sh} decreased significantly to 28.5 kΩ/sq, R_C to 910 Ω and ρ_C to 5x10^{-3} Ω-cm^2. The considerable decrease in electrical resistance is likely due to the reduction in adsorbed species (photoresist and solvent residue, oxygen etc.) present on the bare graphene surface [1]. The effect of thermal treatment on the oxygen functional groups was studied by Raman spectroscopy, which showed the presence of the D-peak with only a small decrease in I_D/I_G ratio from 1.06 to 0.85 (Fig. 2c). In addition, Hall measurements showed p-type behavior was maintained; in combination, both measurements indicate that the temperature range studied here does not substantially change the structural or electrical character of functionalized graphene films.

In order to examine the performance and the stability of oxygen functionalized graphene/metal contact interfaces, electrical measurements were performed at temperatures between 300 K and 673 K in an ambient atmosphere. The initial measurements were taken at 300 K and recorded every 50 K rise in temperature to up to 673 K. As shown in Fig. 4, a 75% drop in R_C was observed from 900 Ω at 300 K to 220 Ω at 673 K. This decrease can be attributed to the enhancement of thermally generated electron-hole pairs and an increased carrier transmittance across the interface [5]. A 33% drop in R_{sh} was observed from 27 kΩ/sq (300 K) to 18 kΩ/sq (673 K) as shown in Fig. 5. This behavior is similar to typical semiconductors, where electrical resistance decreases with increasing temperature due to the growing concentration of thermally generated free carriers. When the same measurements were repeated two times, no significant deviation in R_C or R_{sh} was observed, further demonstrating the stability of the device at extreme temperatures.

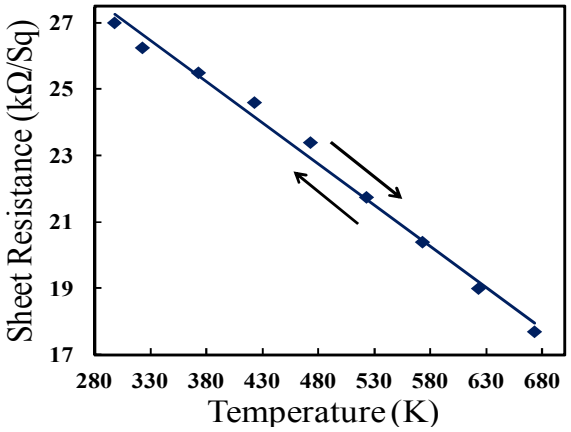

Fig. 5. Oxygen functionalized epitaxial graphene sheet resistance as function of temperature.

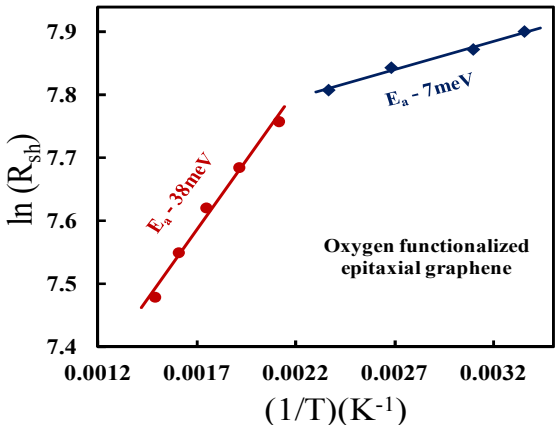

Fig. 6. Plot of Sheet resistance vs 1/T for oxygen functionalized epitaxial graphene showing two Arrhenius like behaviors.

Fig. 6 shows that the sheet resistance of oxygen functionalized graphene as a function of 1/T possesses two activation processes, where the electron transport mechanism at low temperatures has a very small activation energy (E_a) of 7 meV, but a sharp change in slope was observed at about 473 K with an estimated E_a of 38 meV. The existence of two different behaviors may be attributed to two different localized states associated with the functional groups. Further studies are required to understand the exact transport mechanism at functionalized graphene and metal contact interfaces.

Summary

The stability of oxygen functionalized epitaxial graphene/metal contact interfaces were investigated at high temperatures. The electrical characteristics showed a 75% decrease in contact resistance and a 33% decrease in sheet resistance when the temperature was increased from 300 K to 673 K. The sheet resistance showed Arrhenius-type behaviour for functionalized graphene films with activation energy of 7 meV near room temperature and 38 meV at elevated temperatures. Structural, chemical and electrical analysis showed the thermal stability of the device and the robust nature of metal contacts at temperatures up to 673 K.

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